

UNDERGRADUATE HONORS THESIS

“Effect of Complex Loading History on Strain-induced crystallization in poly(ethylene terephthalate) (PET)”

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Abstract

Strain induced crystallization in PET has been studied extensively under simple, constant strain, loading conditions. By implementing the addition of a hold into the deformation process PET will have the additional needed time to crystallize. Plane strain and uniaxial compression tests on small PET specimens will be utilized to gain a better understanding of the crystallization characteristics throughout the deformation process.

Introduction

Polyethylene terephthalate (PET) and polyethylene terephthalate-glycol (PETG) are some of the most widely used plastics in industry today and have a vast amount of applications that require them to be very strong. This project involves conducting experiments on PET and PETG to analyze their relationship to each other as well as their crystallization characteristics. PETG is actually a copolymer of PET and generally does not crystallize. The main purpose for testing PETG is for benchmarking data and comparison purposes. The rationale behind understanding these relationships is very significant. If a model is obtained that shows a method of deforming the material in such a way that the strength actually increases, then less material could be used and the same load capacity could still be achieved. This would have enormous implications in industry and would save companies who use the material millions of dollars.

The strength of the polymer will increase as it crystallizes. When the polymer is heated the molecular chains move more easily and less force is needed for deformation. As the polymer deforms, the chains of molecules become more aligned and can start to crystallize. By changing the temperature, strain rate and hold times an optimal process of deformation resulting in crystallization and thus an increased strength will be found. Virtually all commercial grades of

PET have a small amount of additives in the material mostly for different types of manufacturing processes. Throughout these experiments two different grades of PET will be used and both are commercial grade. One is a more “pure” form of PET and will be referenced for the remainder of the paper as PET00 because there are virtually no additives mixed into the material. The other grade is very common having some additives and will be referenced just as PET. Experiments have already been conducted for changing temperatures and strain rates for both polymers. This experiment will investigate the effect that hold time has in the polymer deformation process.

Experimental procedure

The experimental set up and testing procedure are similar to the set up used by Greg Palm [3] except with the added variable of hold time. This allows a comparison to be done between the data that will result from this project and existing data. Different sets of uni-axial compression tests were conducted on PET, PET00 and PETG. Results of the specimens before and after compression testing deformation are shown in Figure 1.

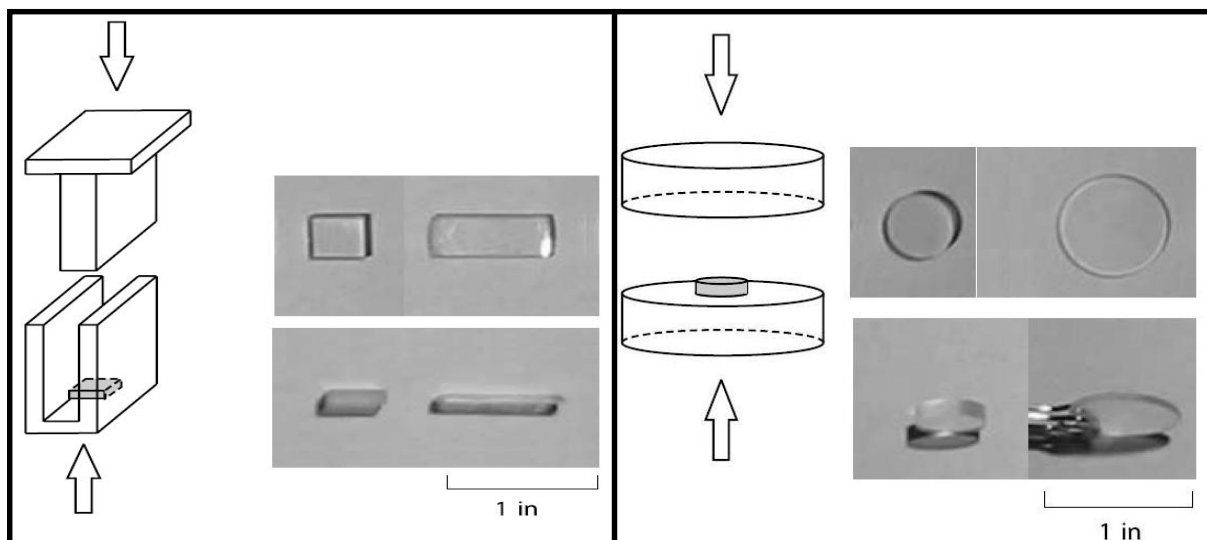


Figure 1: Plane strain and uniaxial experimental set up and deformed pieces [1]

Each uni-axial specimen has been machined to have a diameter of approximately 12.4mm and a height of 3.2mm, the plane strain specimens have been machined to have a height of 3.2mm, length and width of 10mm. The specimen is kept in a desiccant chamber to eliminate the absorption of water due to the fact that over time the material can absorb water, which affects the mechanical behavior. Prior to starting the experiment the heat controlled test chamber must first be heated to the desired temperature, test chamber shown in Figure 2.



Figure 2: Temperature controlled chamber

To ensure even heating of the specimen several precautions are taken. First, the chamber is heated for at least two hours to ensure the metal platens have also reached the set temperature. This is done so that there is an even distribution of heat transfer between the specimen, the surrounding air and the metal platens. Another precaution taken to ensure uniform temperature in the specimen is a pre-determined annealing time for each specimen. Before starting the test, each specimen is placed into the heated chamber into a testing ready position for 15 minutes to

ensure the entire specimen has reached the target temperature. This ensures uniform temperature of the specimen. The natural response of the material is to relax as temperature is increased so it is very important to have the entire specimen at a uniform temperature to ensure uniform deformation.

For each different set of tests a different variable is changed, strain rate, temperature and hold time respectively. The next set of experiments is conducted utilizing a plane strain device (Figure 3).



Figure 3: Plane Strain testing device

The polymer chains have a tendency to crystallize even more when the direction of deformation is confined to only moving in one plane. Therefore, conducting the plane strain experiments allows for a greater understanding of the strength and crystallization properties due to complex loading histories. The testing procedure for the plane strain tests will be identical to the uni-axial experiments with the plane strain device going through the same 15 minute period of time to reach the target temperature with the specimen already placed inside, ready for testing.

The results will hopefully follow the predictions of the theoretical model that has been created (Figure 4).

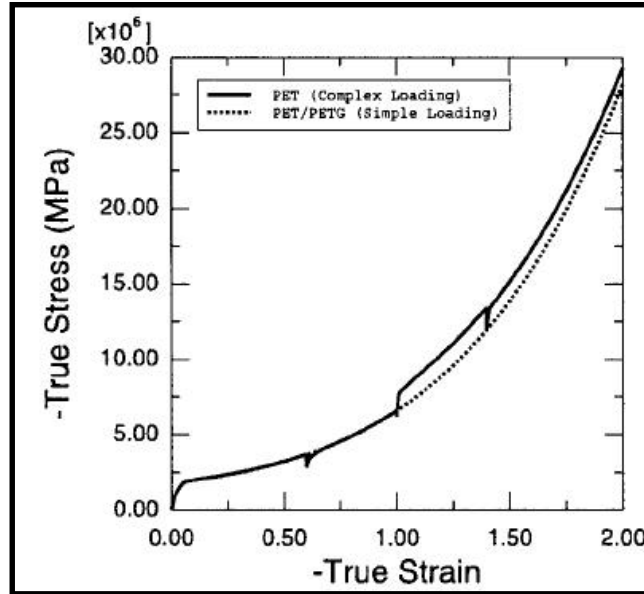


Figure 4: Theoretical model of complex loading history for PET/PETG [2]

After a series of complex loadings on the polymer, the stress-strain curve should be stiffer compared to a simple loading deformation process. This increase in stress-strain behavior is due to an increase in the crystallization in the polymer. After all testing is completed, the results will be put together to locate the parameters necessary for maximum polymer crystallization which will result in maximum strength.

Experimental Results

All experimental results refer to uniaxial compression tests unless otherwise noted

All strains, stresses and strain rate values are in compression

Figure 5 shows PETG at 90°C with different hold times at a strain rate of 0.005/sec.

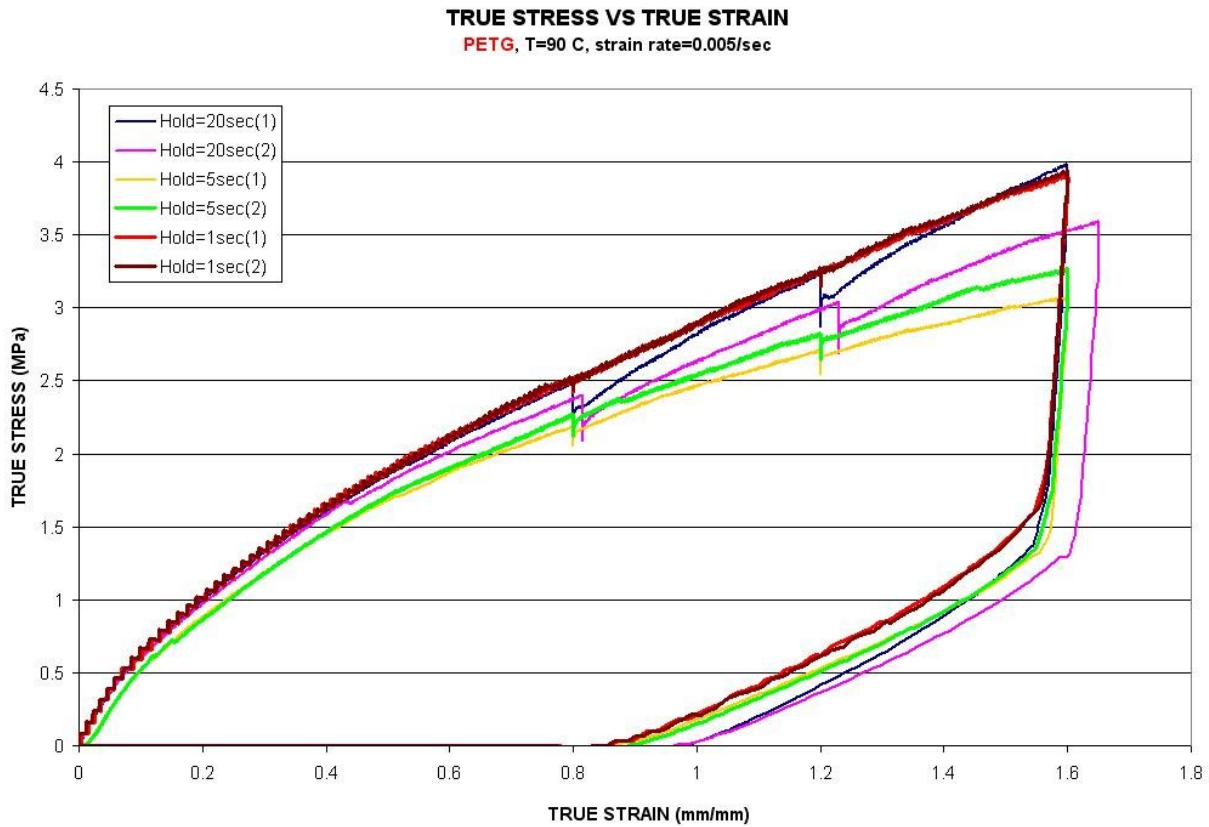


Figure 5: True Stress vs. True Strain, PETG, T=90C, strain rate=0.005/sec

The different hold times coincide with the strains of 0.8, 1.2 and 1.6 respectively. These strains are used throughout the experiment with corresponding holds. PETG is analyzed first so as to establish a baseline for comparison to PET. The experiment run with only a one second hold is shown by the red and brown lines and does not deviate from the linear path of the stress strain curve at all. While there is some difference in the final maximum stress induced on the specimen

it is not very significant. For the longer hold times, five and twenty seconds, the stress decreases during the hold but then resumes the expected path of the stress-strain curve. There are no significant implications of the hold time for this combination of temperature, strain rate and hold times. Even though both trials with a hold time of five seconds ended up with the lowest final stress the trials with a twenty second hold time shown by the blue and purple lines achieve very similar stresses as the trial with only a one second hold. The lowest final stress occurs when the specimen has lower stresses throughout the experiment. As seen in the figure both trials with a five second hold time have the lowest final stresses but also start off with smaller stresses before the first hold.

Because of the small differences in material composition or other small variables which result in small differences in stress in the material it is interesting to look at the relative difference in stress between each hold. The stress values taken for all of the relative stress-strain graphs are measured directly before the hold begins at each corresponding strain. Figure 6 displays the same data as Figure 5 except with values relative to the measured stress at the first hold.

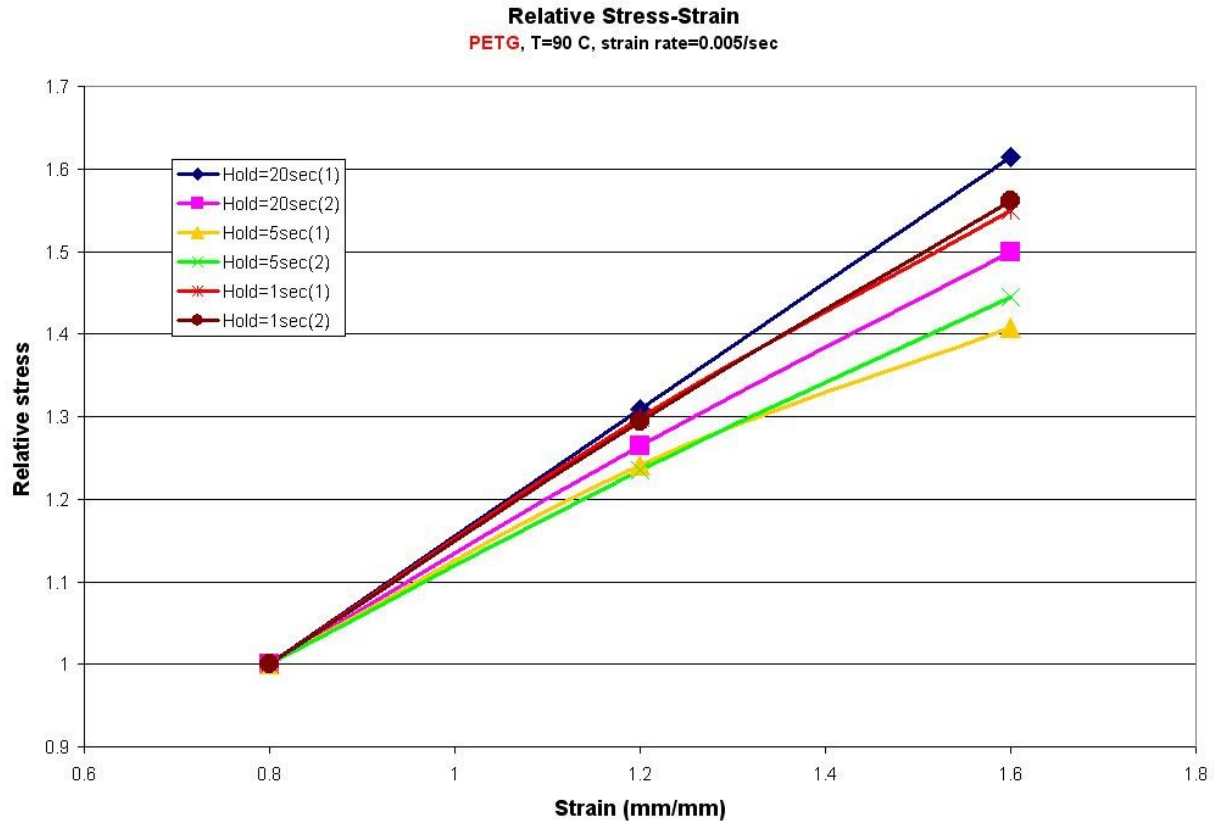


Figure 6: Relative True Stress vs. True Strain, PETG, T=90C, strain rate=0.005/sec

Obviously each relative stress value at the first hold time is equal to one because it is relative to itself. The stress values at the strain rates of 1.2 and 1.6 are just the stress measured at the corresponding strain divided by the stress measured at a strain of 0.8. This graph helps show how the hold actually affects each material. As seen in this figure there is no significant impact of the different hold times. Each relative stress is close to each other. This is to be expected since this is PETG.

More tests were conducted using PETG at the same temperature, 90°C with different hold times but this time a strain rate of 0.05/sec. These results are shown in Figure 7 below.

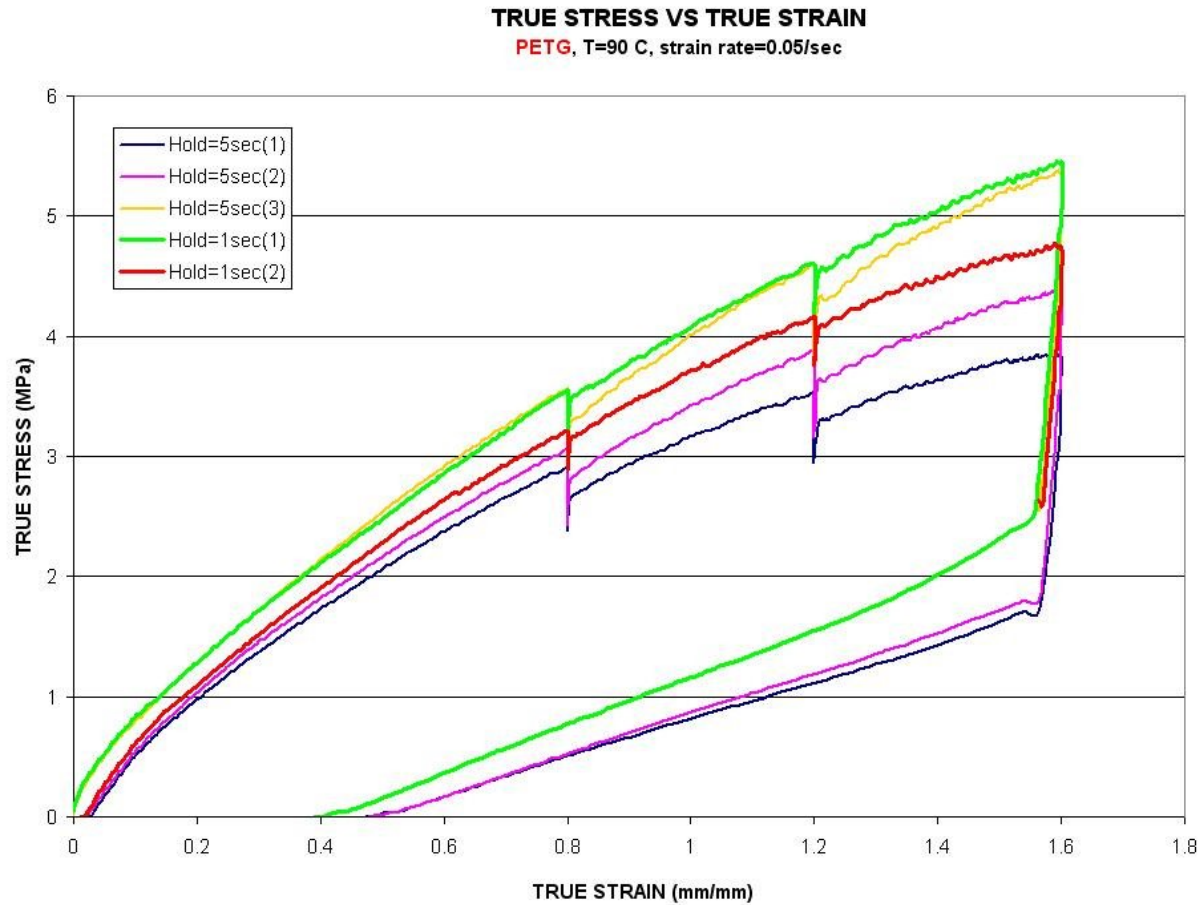


Figure 7: True Stress vs. True Strain, PETG, T=90C, strain rate=0.05/sec

As can be seen in the figure there are no significantly different trends between the specimens with different hold times. The trials with lower final stresses also started with a little lower stress. This is due to the initial loading of the material. As described in the experimental procedure these specimens were not in direct contact with the platens at the very start of the trial. The relative stresses after the holds for this data is shown in Figure 8.

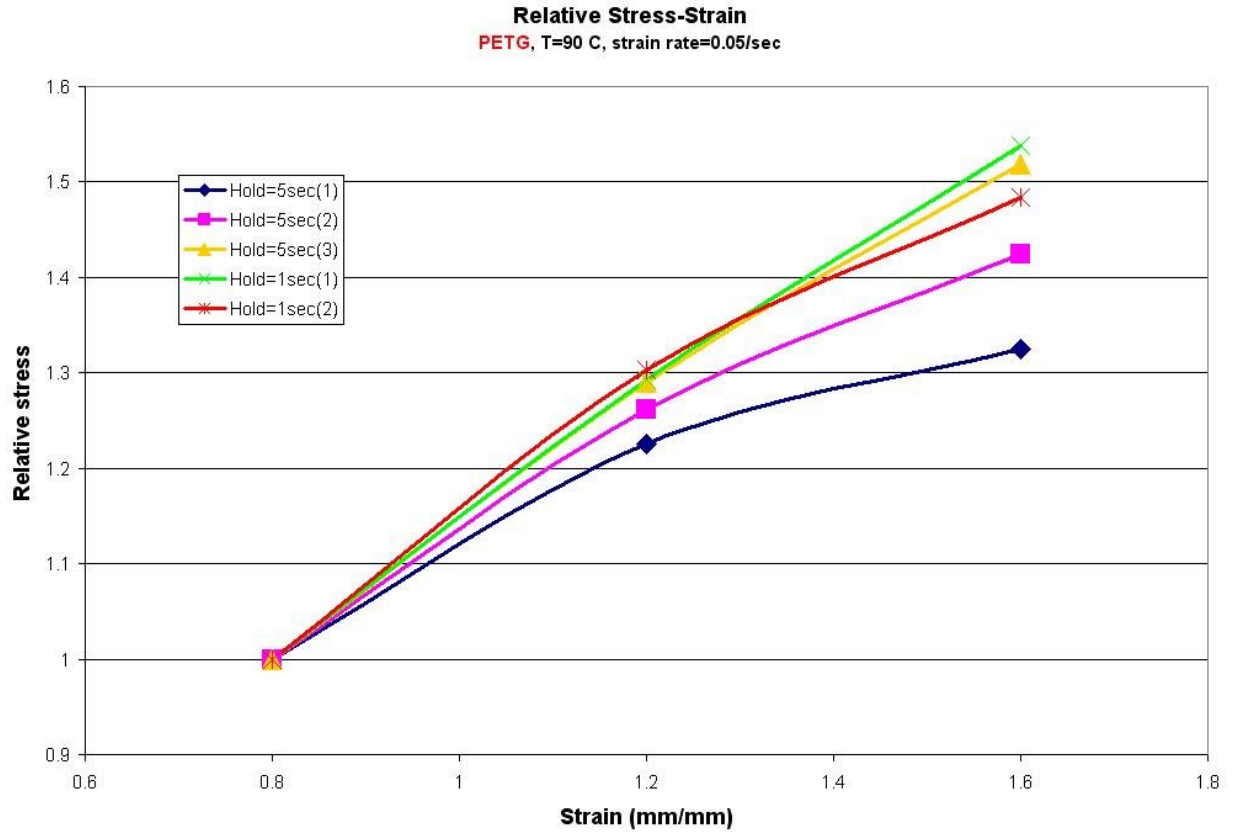


Figure 8: Relative True Stress vs. True Strain, PETG, T=90C, strain rate=0.05/sec

As observed in the figure there is no significant difference between materials after the hold times. The trials which started their deformation a little later (5sec(3), both 1sec trials) also ended up with a little bit lighter final relative stress.

Figure 9 shows PETG tested at 100°C with a strain rate of 0.005/sec.

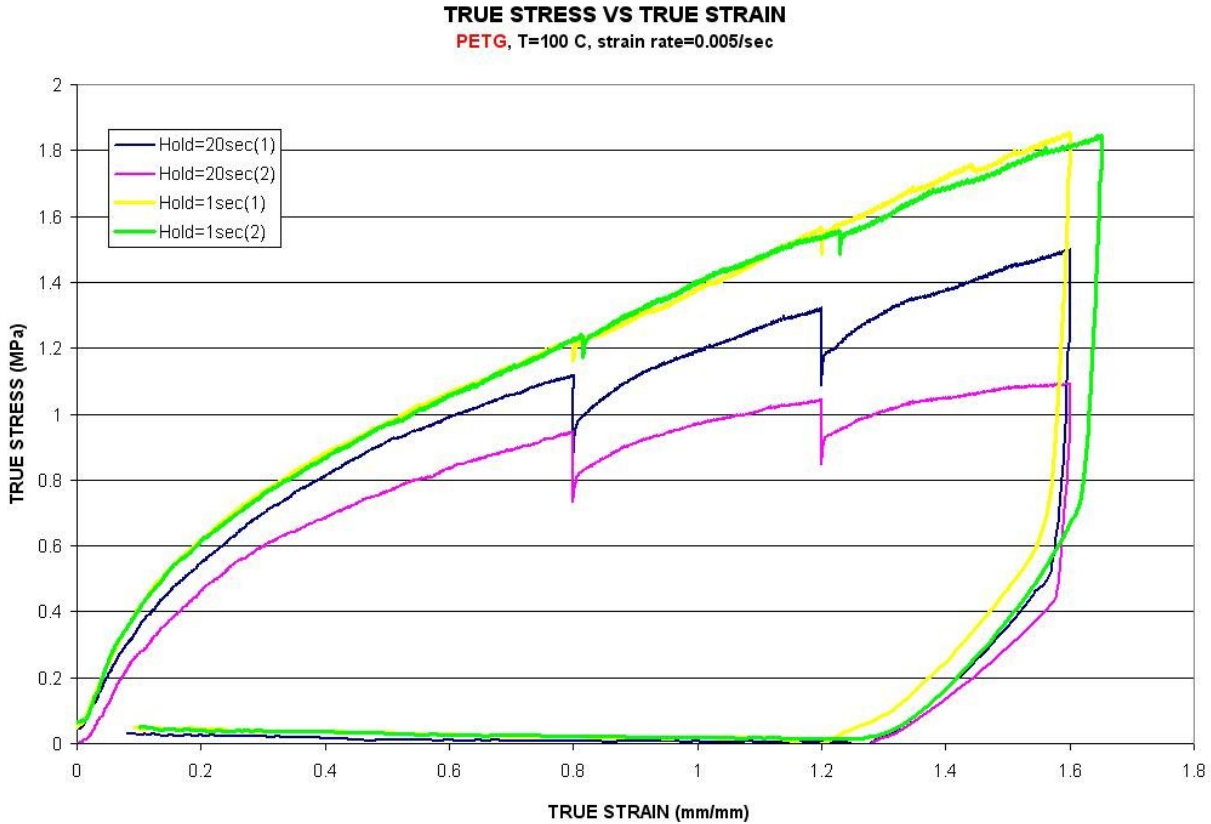


Figure 9: True Stress vs. True Strain, PETG, T=100C, strain rate=0.005/sec

As can be seen from the picture the material relaxes even more during the 20 second hold times and does not reach as high of stresses compared with the 1 second hold time tests. Both trials with hold times of 20 seconds start out with lower stresses, as seen in the figure, before the first hold at a strain of 0.8. It is also interesting to notice with the 20 second hold time tests the amount of relaxation that occurs in the specimen during the hold. With only a one second hold the stress in the specimen quickly gets back on track with the projected profile whereas after the 20 second hold the specimen relaxes greatly. When the deformation continues after the 20 second hold the material is under less stress for a significant amount of time. Similarly to the analysis of the PETG at 90° C it is beneficial to look at a relative value of stress compared to the initial strain hold. The relative stresses from Figure 9 are shown below in Figure 10.

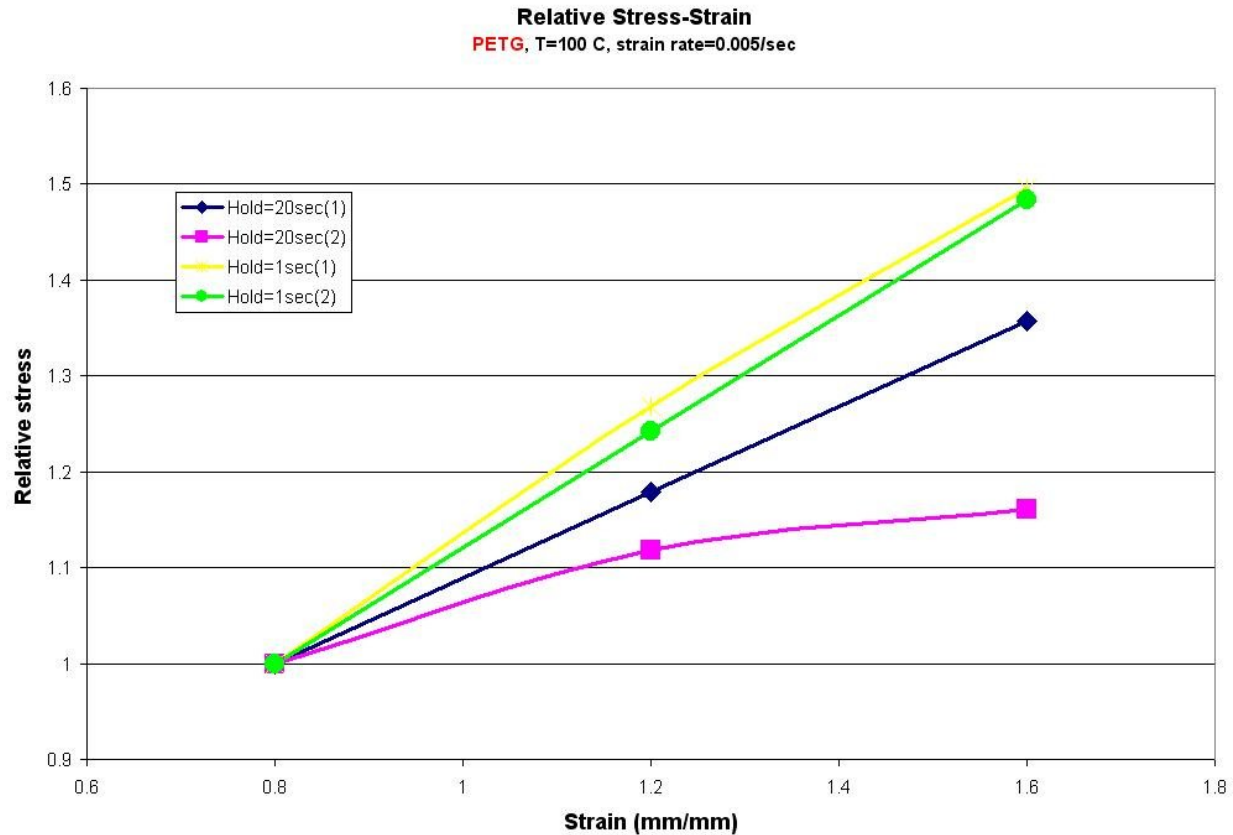


Figure 10: Relative True Stress vs. True Strain, PETG, T=100C, strain rate=0.005/sec

As can be seen in the figure, both trials with the longer hold time of 20 seconds have a lower relative stress after their hold times. This is not a dramatic difference and is not conclusive as to whether or not the longer holds result in a lower relative stress but it might be a trend. Having a hold time of 20 seconds for an experiment significantly increases the total testing time compared to only a one second hold and this could definitely impact the lower stresses in the specimen with longer hold times.

A comparison between the PETG tested at 100°C and 90°C is shown in Figure 11.

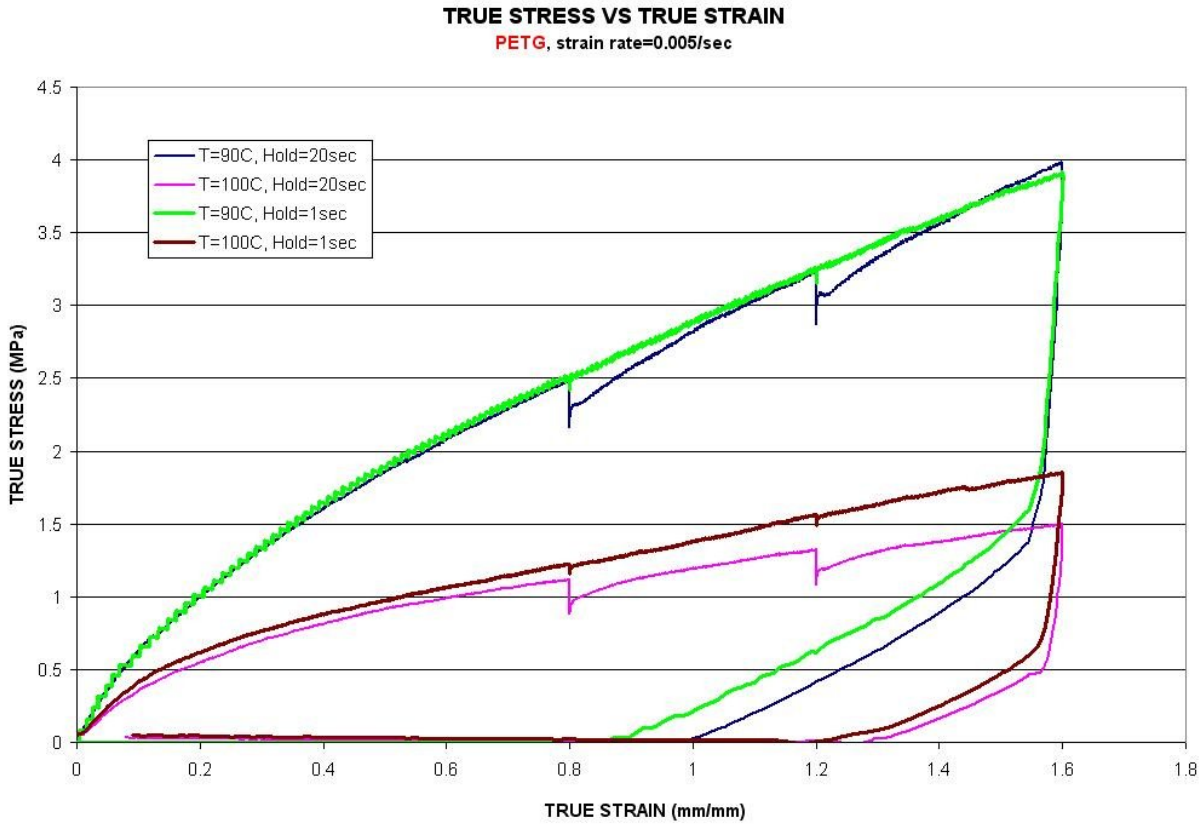


Figure 11: True Stress vs. True Strain, PETG, strain rate=0.005/sec

This figure clearly shows the differences between the two temperatures. With only a ten degree increase in temperature the stresses are cut in half. The relative stress comparison between the two temperatures is shown in Figure 12.

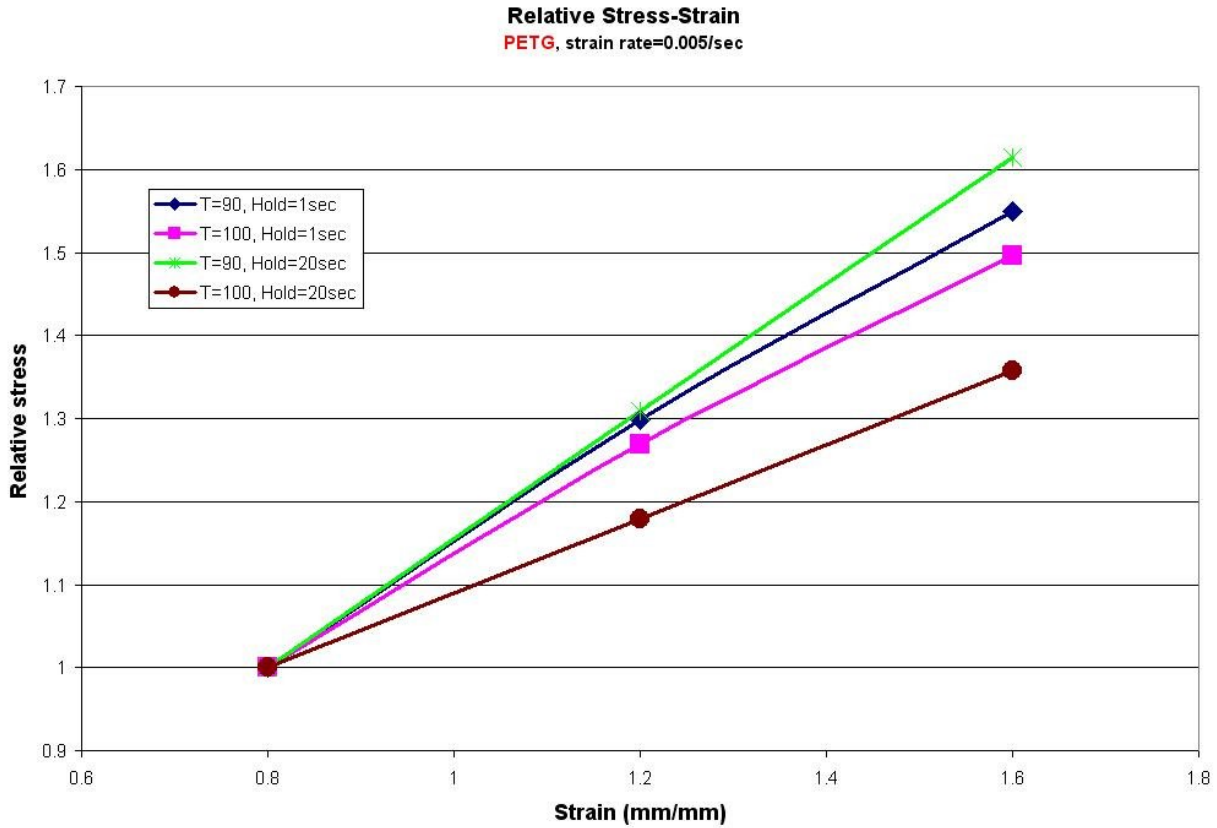


Figure 12: Relative True Stress vs. True Strain, PETG, strain rate=0.005/sec

As seen in the figure the lower temperature specimens have a little higher relative stress as strain increases.

Figure 13 shows PET and PET00 at 90°C with a hold time of five seconds compared to PETG, each material tested at a strain rate of 0.05/sec.

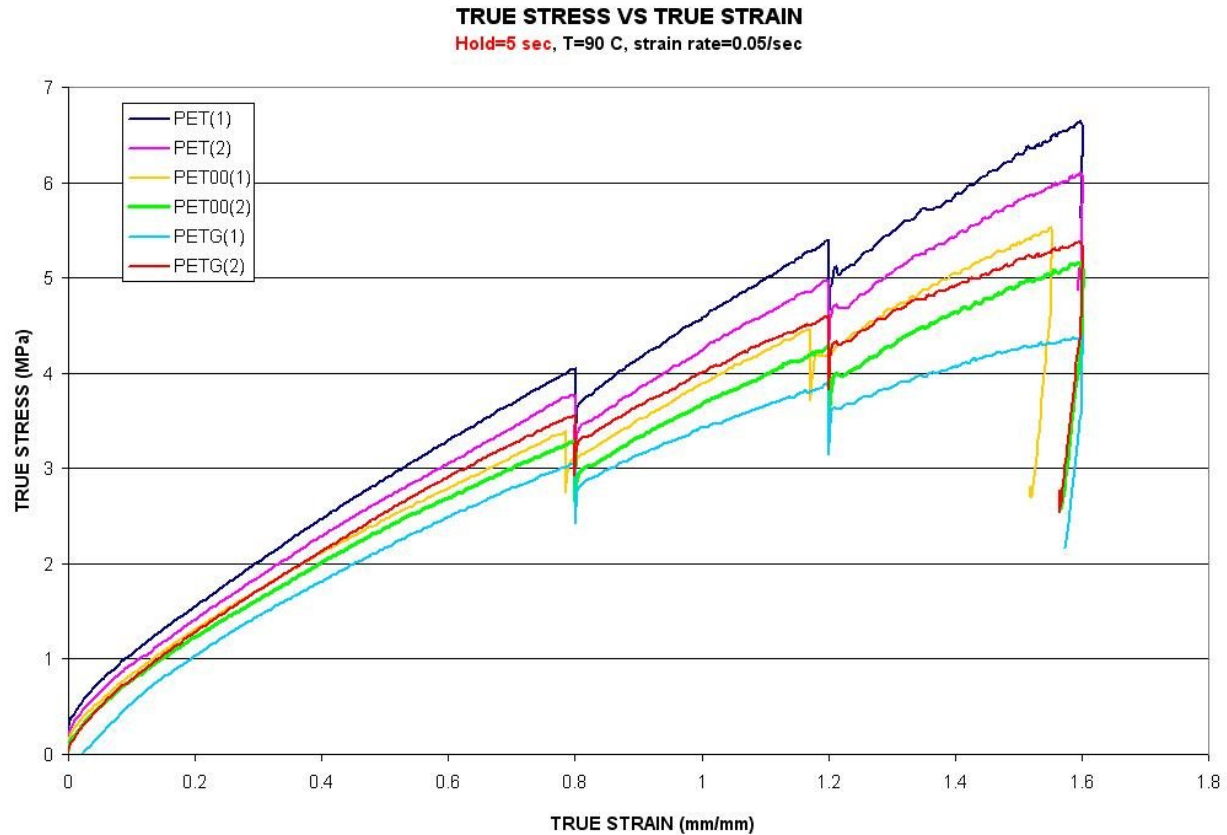


Figure 13: True Stress vs. True Strain, hold=5 sec, T=90C, strain rate=0.05/sec

This figure shows how there are no significant differences in any of these materials using this uniaxial testing. With a hold time of 5 seconds this figure shows the relaxation of each specimen during the hold. The differences in final stress is not significant and can be due to the error in the start of the tests and when deformation actually starts as well as minor material differences.

The relative stresses for this data are shown in Figure 14.

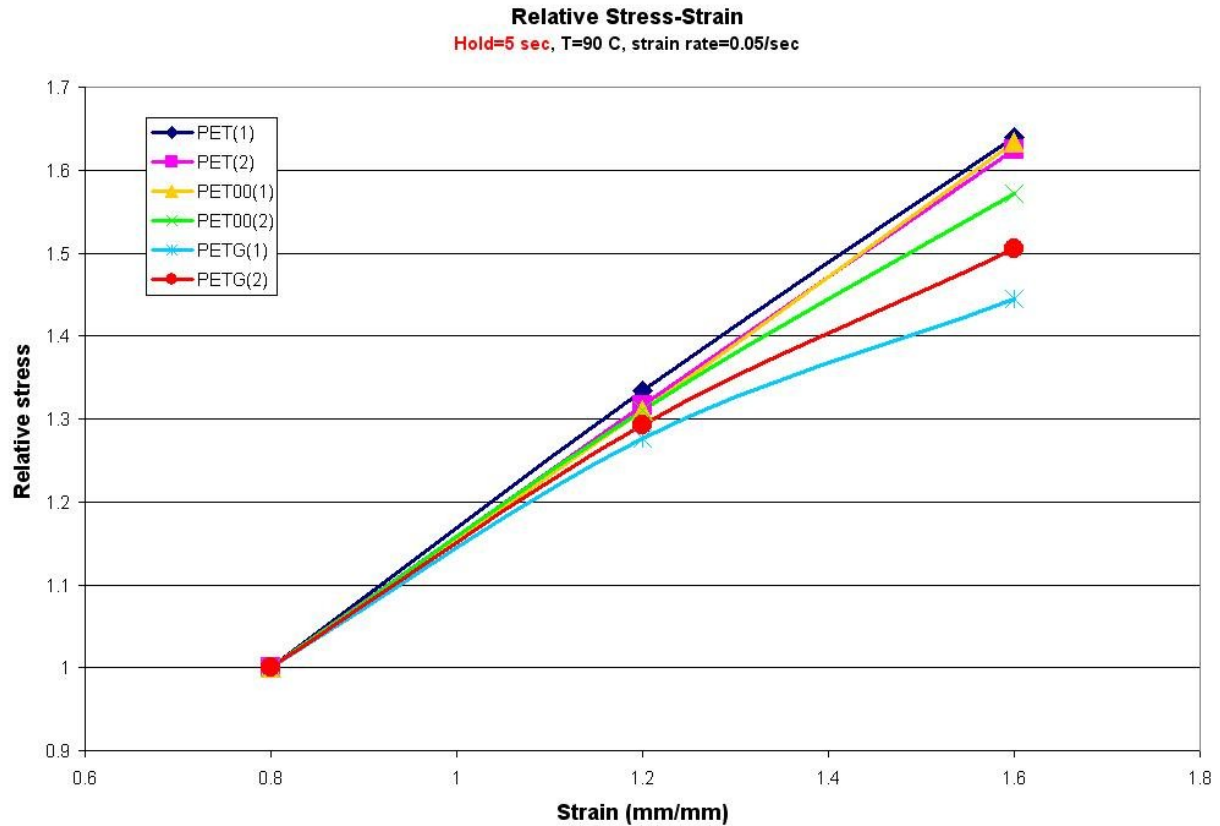


Figure 14: Relative True Stress vs. True Strain, hold=5sec, T=90C, strain rate=0.005/sec

As seen in this figure all the materials have virtually the same reaction to the hold without significant differences between materials after the hold.

To analyze the crystallization characteristics better a more extreme case of PET is tested at 100°C with hold times of 5 and 20 seconds. PET will crystallize easier at this temperature because it's further above its glass transition temperature of 80°C. The results are shown in Figure 15.

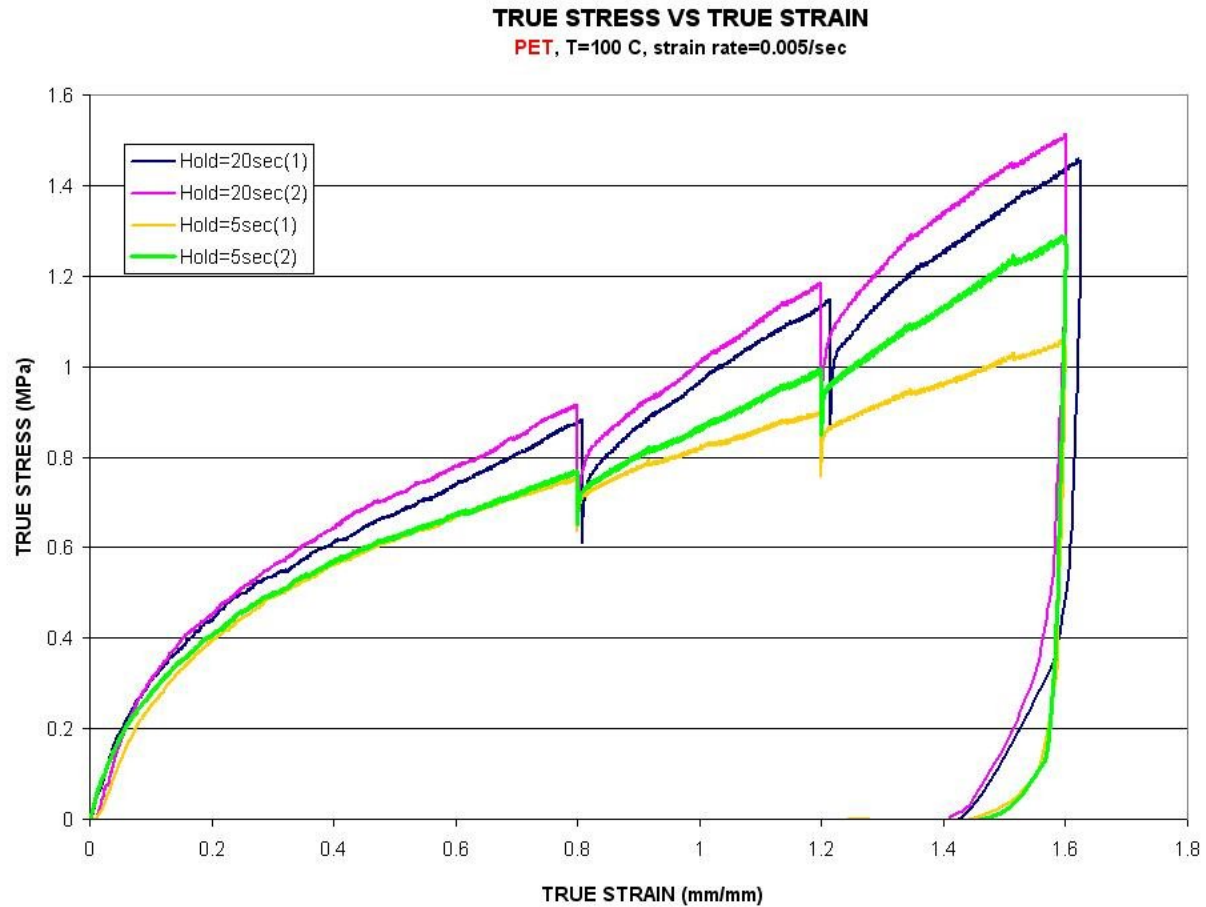


Figure 15: True Stress vs. True Strain, PET, T=100C, strain rate=0.005/sec

This figure shows the difference in relaxation for the material with the longer hold time but no significant difference in stress due to the holds. Although both the 5 second and 20 second hold time trials are tested at the same strain rate they do not identically follow each other to the first hold. There is not a large enough difference to imply anything significant other than some sort of material or process difference between the two trials. The relative stress values for this data are shown in Figure 16.

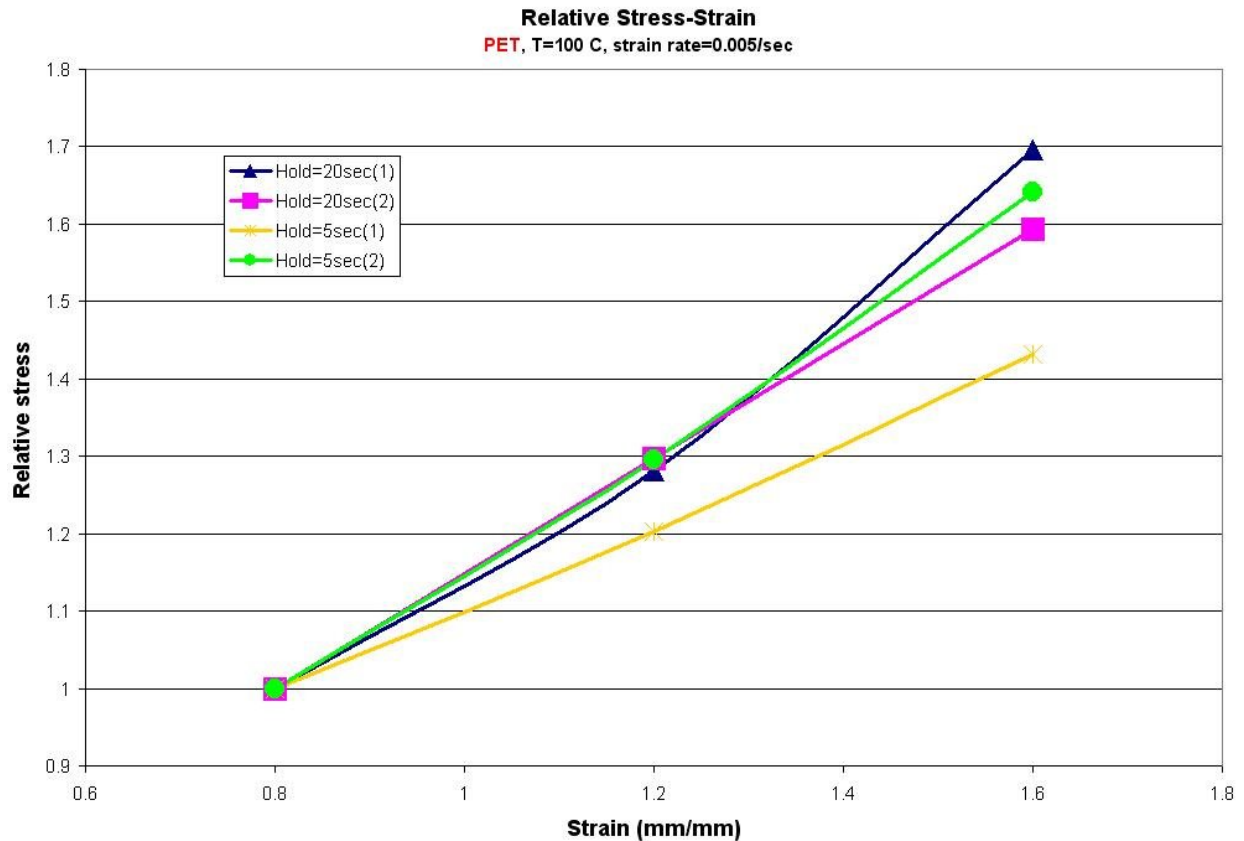


Figure 16: Relative True Stress vs. True Strain, PET, T=100C, strain rate=0.005/sec

As seen in the figure there is no significant difference between the different hold times.

Although the first trial with the five second hold is lower than the other trials it still follows the general trend of increasing relative stress. While there does not appear to be much affect of the holds in this process it is also valuable to compare materials at the longest hold time, 20 seconds and 100°C , a higher temperature than when materials were compared earlier in Figure 13. This material comparison is shown in Figure 17.

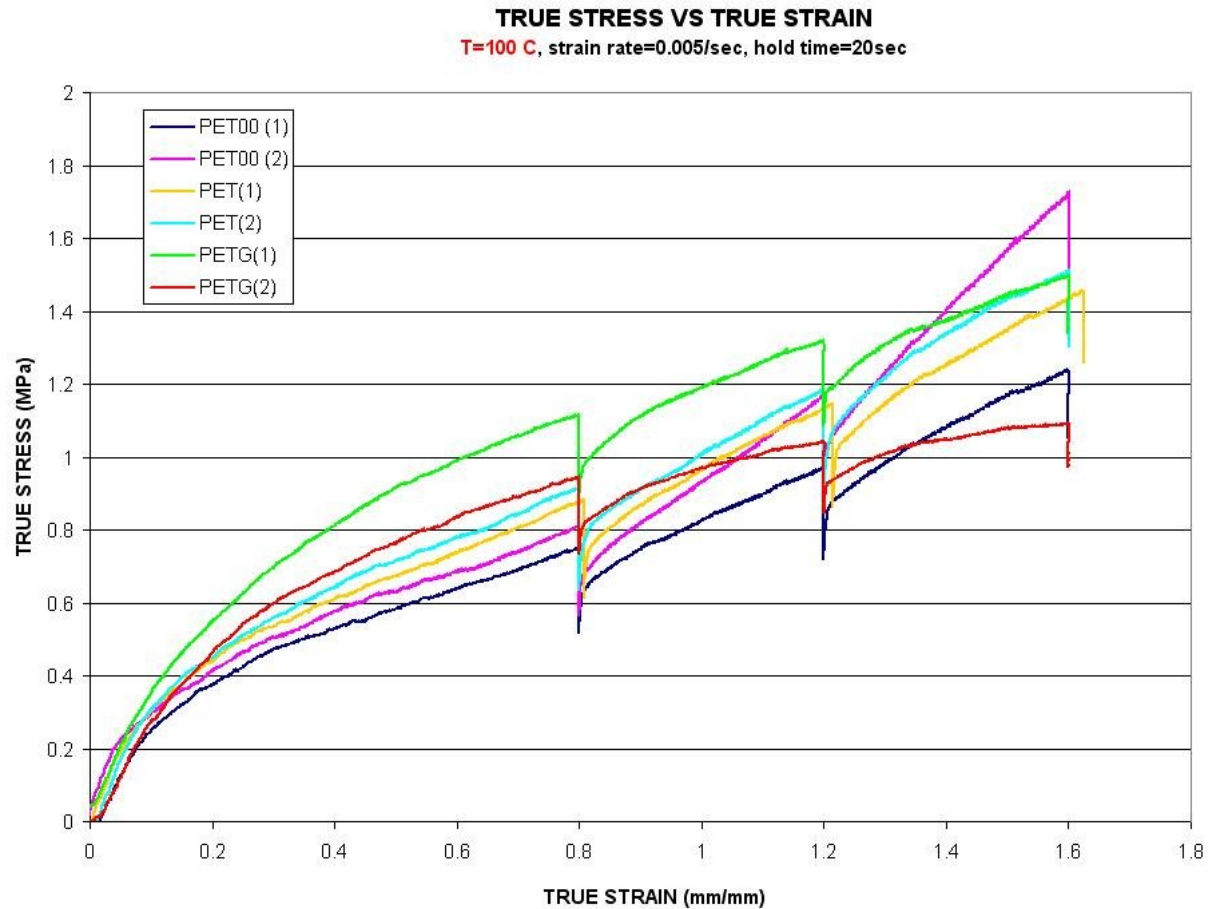


Figure 17: True Stress vs. True Strain, hold=20 sec, T=100C, strain rate=0.005/sec

As seen in the figure there really is not a significant amount of difference between the stresses incurred in each different material. Similar to the other figures, this also shows the relaxation in stress for each material during the hold. The relative stresses for this graph are shown in Figure 18.

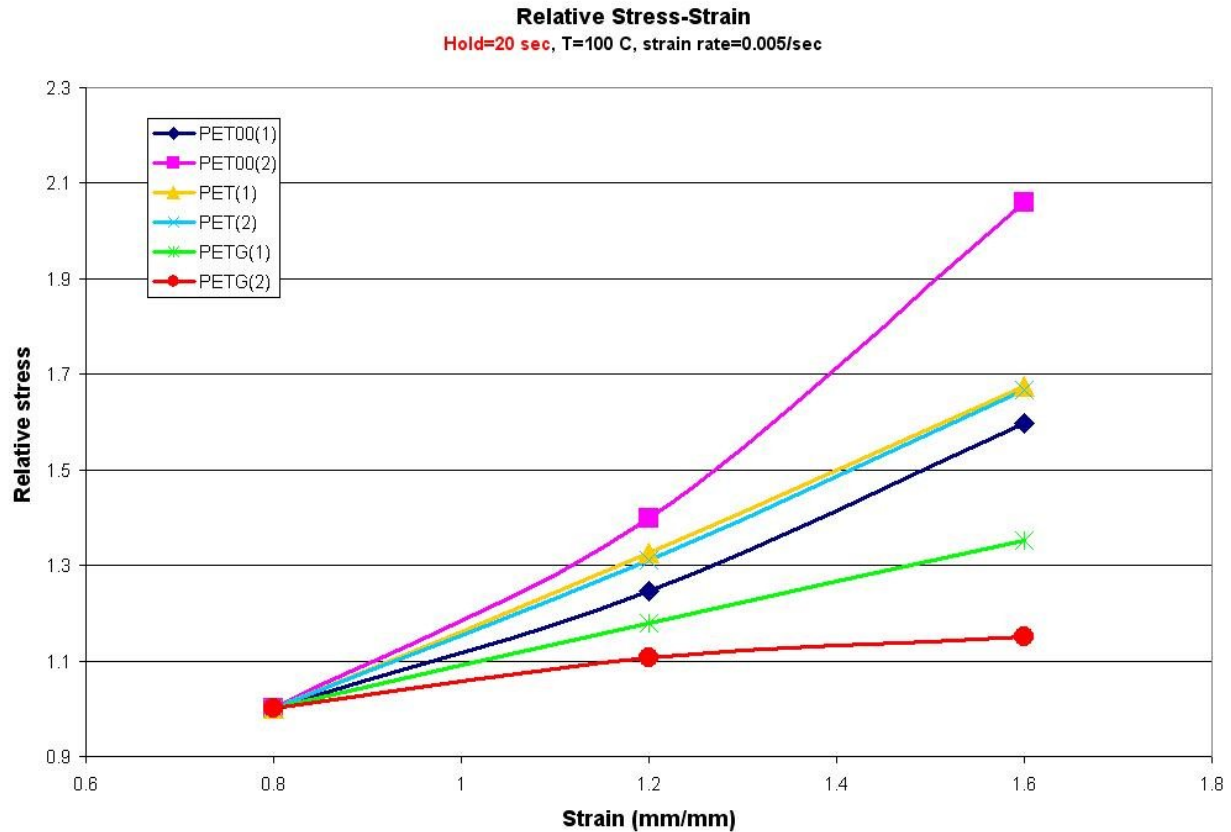


Figure 18: Relative True Stress vs. True Strain, hold=20sec, T=100C, strain rate=0.005/sec

It appears from this figure there may be a trend starting to appear. Each PET and PET00 relative stresses are higher than the PETG relative stresses after the holds. The second trial with the PET00 shows an even greater increase in stress from the second to the third hold. This could possibly be due to an increase in crystallization within the specimen during the hold. It is possible that for the uniaxial case this combination of hold time and temperature is close to a threshold of increasing crystallization within the specimen but this current test is not conclusive.

Next to be analyzed is the plane strain testing. Since many of the relationships between material and various hold times have already been done in the uniaxial case there will only be a few cases of plane strain testing that will be analyzed. Figure 19 displays the data from testing PET00 at 90° C with a strain rate of 0.005/sec with no hold and a 20 second hold.

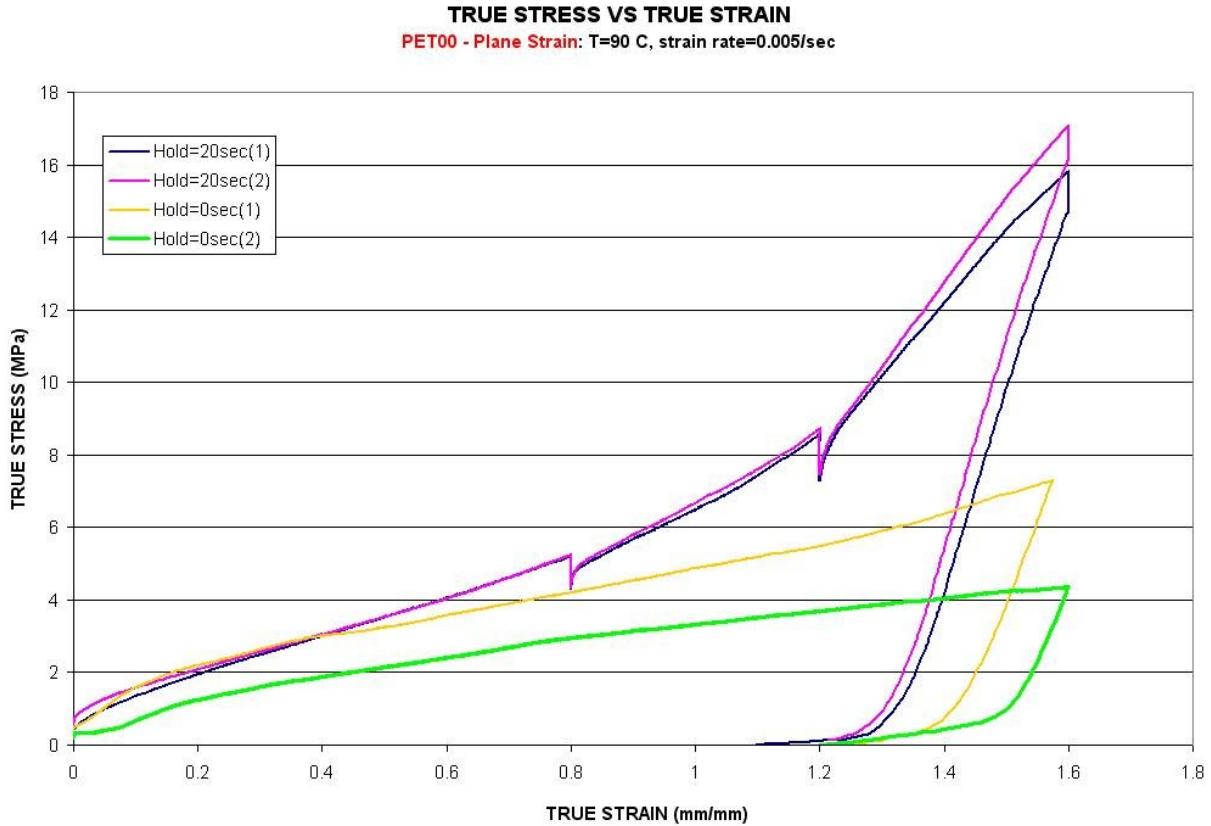


Figure 19: True Stress vs. True Strain, plane strain, PET00, T=90C, strain rate=0.005/sec

As can be seen in the figure there appears to be a clear difference in material behavior between these two processes. While both tests were relatively close in stress incurred in the material up to the first hold, afterwards they are quite different. The hold appears to allow enough time for the crystallization process to occur and increase the stress in the material. The corresponding relative stress graph is shown in Figure 20.

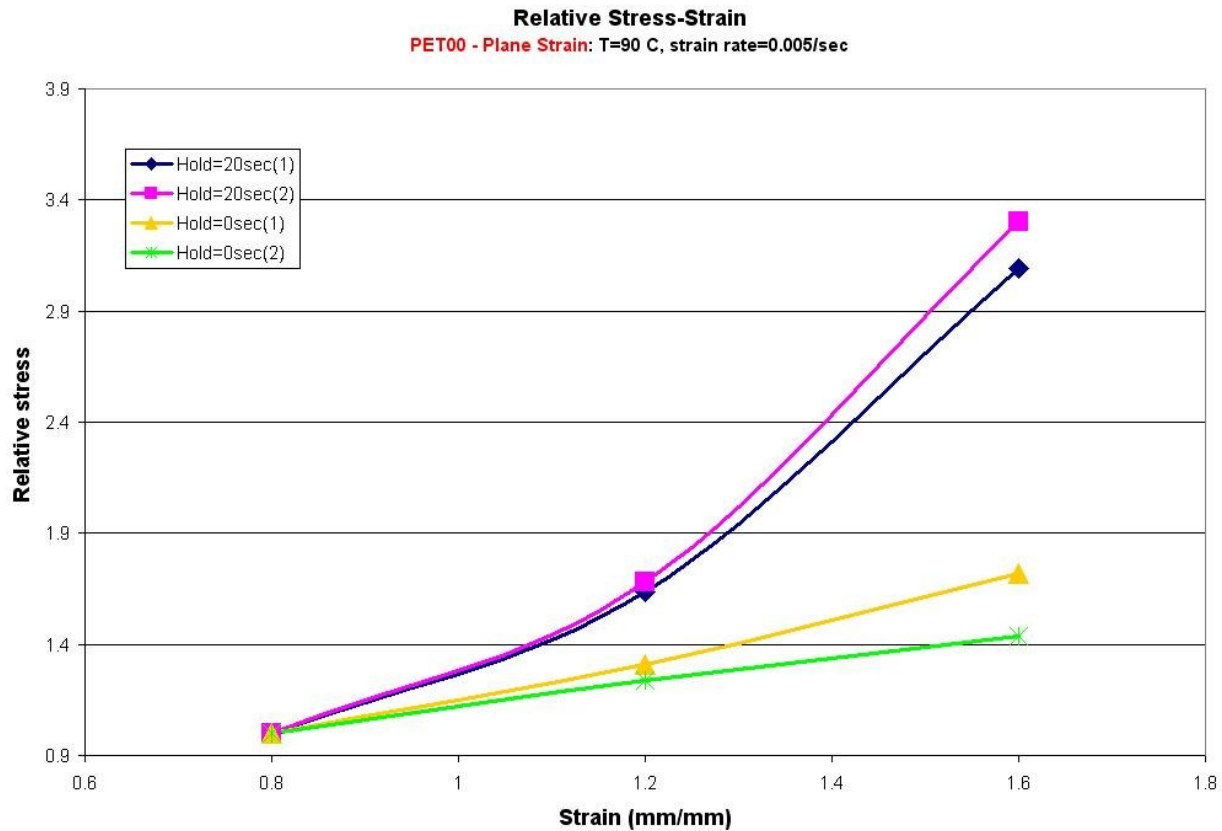


Figure 20: Relative True Stress vs. True Strain, plane strain, PET00, T=90C, strain rate=0.005/sec

As seen in the figure the specimens who underwent a 20 second hold incurred significantly higher stresses after each hold compared to the specimens which did not undergo any holds during deformation at the same strains. There appears to be enough crystallization that even after the first hold the subsequent holds cause an even greater amount of crystallization and stress increase in the specimen.

The process comparison between the two methods of testing, plane strain and uniaxial, is shown in Figure 21. Each case was tested with PET00, at 90°C, a strain rate of 0.005/sec and a hold of 20 seconds.

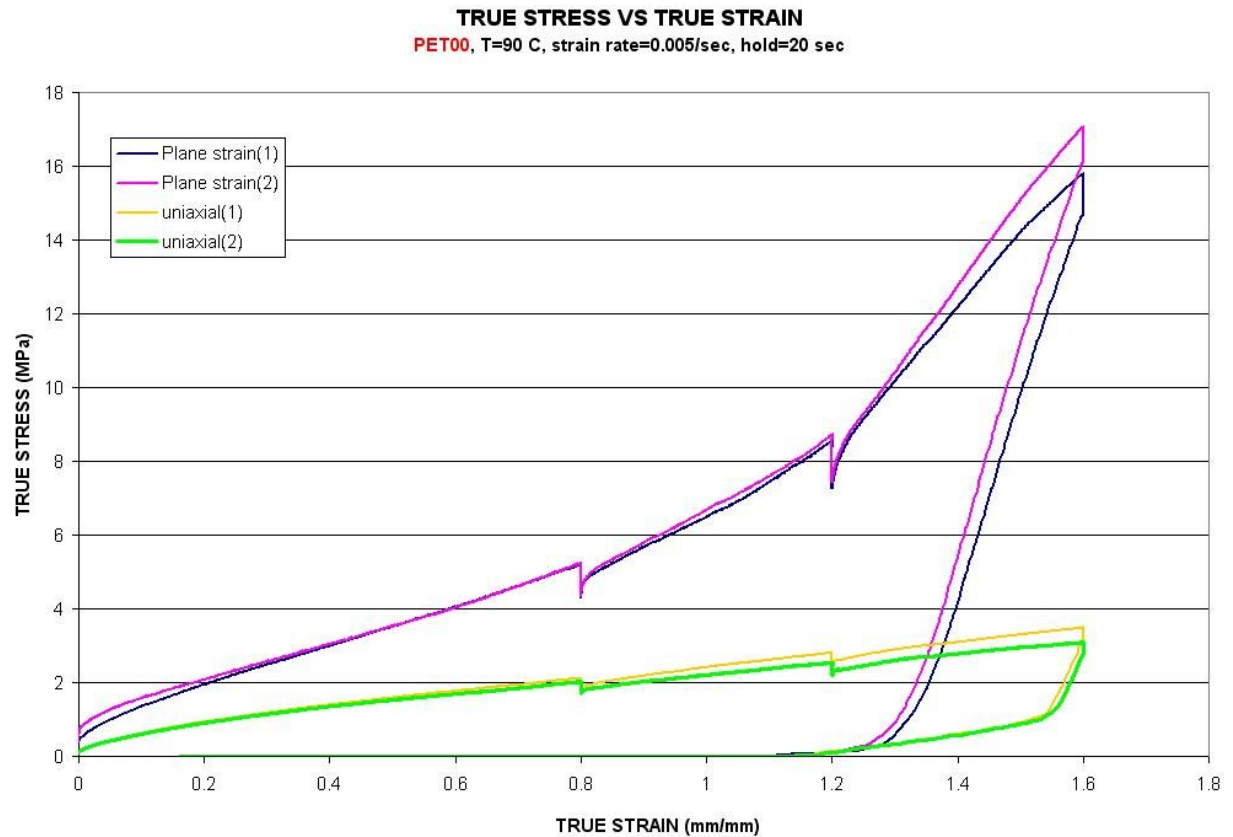


Figure 21: True Stress vs. True Strain, hold=20sec, PET00, T=90C, strain rate=0.005/sec

As seen in the figure the specimen which underwent plane strain deformation experienced significantly higher stresses than the uniaxial case. Not only did the plane strain specimen experience greater stress but after each hold the slope of the curve increases and the specimen incurs an even greater amount of stress. This is more clearly seen in the relative stress-strain curve shown in Figure 22.

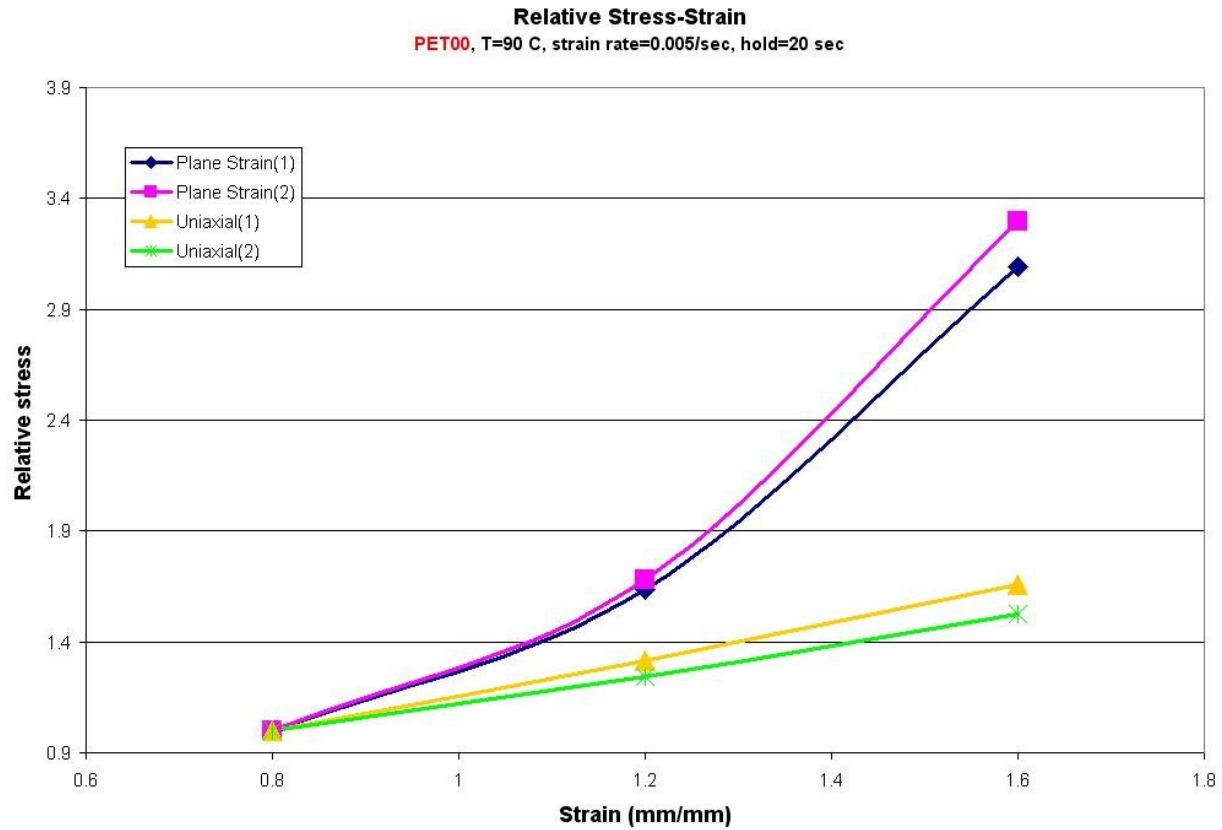


Figure 22: Relative True Stress vs. True Strain, hold=20sec, PET00, T=90C, strain rate=0.005/sec

The plane strain case clearly experiences greater amounts of stress after each hold compared with the uniaxial case. This trend indicates a greater amount of crystallization occurring within the material during the hold causing an increase in stress within the material as the deformation continues after the hold.

Conclusions

There are several conclusions that can be made from the observations made from these experiments. One of the first things that was noticed and stayed constant throughout the experiments was the relaxation that the material experienced during the hold time. The amount of relaxation was seen in the decrease in stress during the hold. On the graphs, throughout the experiment it is clearly seen that at each strain where a hold takes place the stress decreases. During the longer hold times the stress decreased significantly more than during the short hold times. When the deformation continued after the hold the profile of the stress strain curve did not continue directly where it had left off. The material relaxed enough that when deformation continued it did not follow the projection of the stress-strain curve from before the hold immediately, rather the stress slowly increased back up to follow the original projection of the curve.

The combination of strain rates, hold times and temperatures used in this experiment provide inconclusive data to the crystallization characteristics for the uniaxial case of deformation. No significant trends of increases in crystallization were noticed by adding holds into the experiment in the uniaxial case but there were trends in increasing crystallization in the plane strain testing case as seen by the increase in stress after each hold.

Possible future tests could include an analysis of only one hold time at a higher strain to see if the material will crystallize after the hold. Doing this type of experiment would also eliminate the effect of previous holds during the deformation of the material. Another way to test for the crystallization characteristics within the material after deformation could include a wide-angle X-ray diffraction test (WAXD). This would give quantifiable results in regards to the actual amount of crystallization within the specimen.

References

- [1] Dupaix, Rebecca B., Boyce, Mary C., “Finite strain behavior of poly(ethylene terephthalate) (PET) and poly(ethylene terephthalate)-glycol (PETG)”. *Polymer* 46, (2005), 4827-4838.

- [2] Dupaix, Rebecca B., Krishnan, Dwark, “A Constitutive Model for Strain-Induced Crystallization in Poly(ethylene terephthalate) (PET) during Finite Strain Load-Hold Simulations”. *Journal of Engineering Materials and Technology*, (2006) Vol. 128: 28-33.

- [3] Palm, Gregory O., “Large Strain Material Characterization and modeling of Poly(Methyl Methacrylate) (PMMA) Near the Glass Transition”. M.S. Thesis, The Ohio State University, 2005.

Appendix

Error with Instron testing equipment:

After all the testing was completed for this project there were some problems found with the testing equipment being used. The specimens used for testing were so small that they were close to the limits of what the machine could accurately measure in compression. At high strains and more importantly at very high stresses the machine was found to have very significant error in measurement. Most of the testing done during this project was completed at relatively low stresses so the error is not thought to be very large. In future testing, utilizing an LVDT to control the Instron extension profile would be more accurate and allow for more precise controls with small specimens.

Testing Errors/Additional Learning

During the testing of all the specimens it was noted in the experimental procedure section of the paper that proper care was taken to ensure correct and repeatable testing methods. This involved manually guiding the Instron's platens to come into contact with the specimen without actually starting deformation of the specimen. This was accomplished by visually inspecting the load read-out from the computer and lowering the platens into place until the load sensor suddenly increased in value. The sudden increase in load was indicative of the platen compressing the specimen. At first, to ensure that the test started without the specimen being compressed at all initially, after the load increased the platen was backed off just slightly. Doing this caused a greater amount of error into the system because each specimen had the platen raised up off of it slightly but the extension profile the machine was to follow assumed contact from the set point. An example of this is shown below in Figure 23.

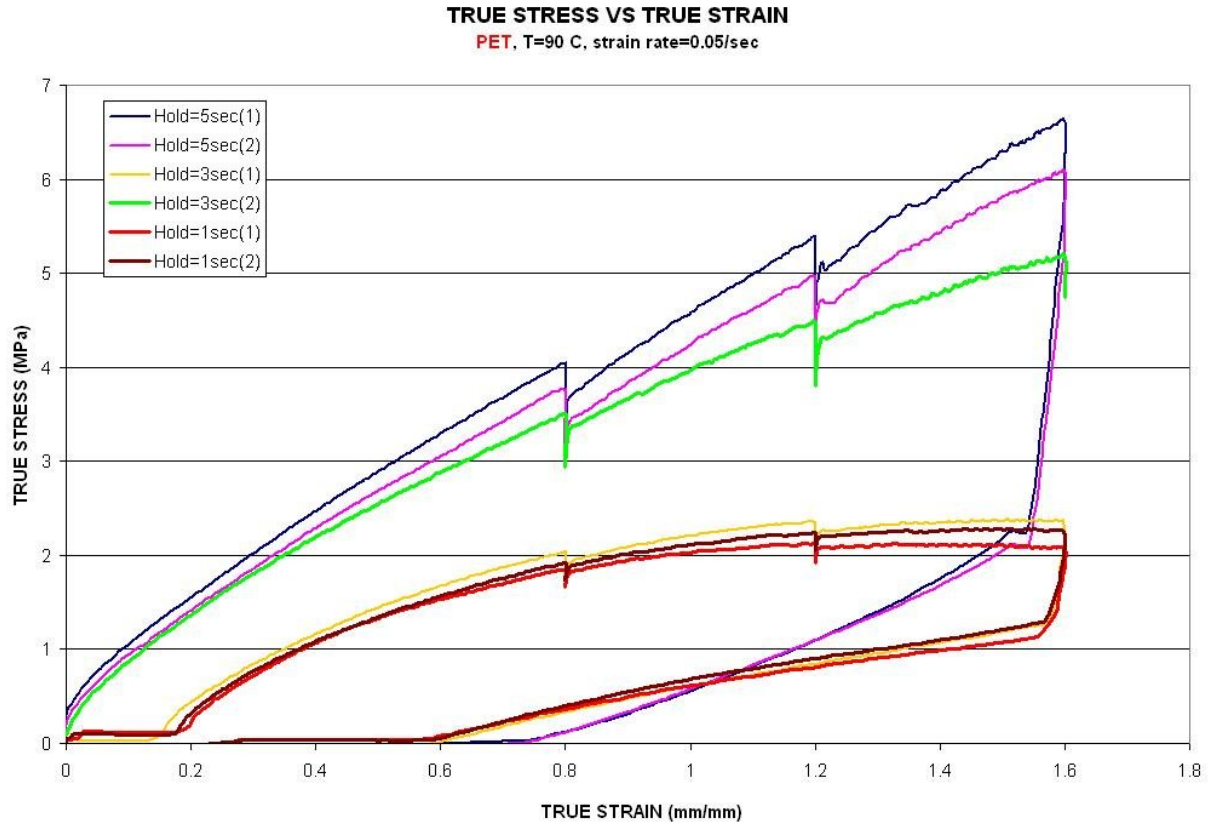


Figure 23: Stress-Strain example of an error in testing

As seen in the figure both 1 second hold time trials and the second 3 second hold time trial do not start increasing in stress until a strain of almost 0.2. This was due to the platen not being directly on the specimen before the test started. The profile that governs the extension of platens changes as strain increases because it's measuring true strain, therefore if the specimen is not actually at the specified strain then it completely ruins the data for comparison purposes. After learning this each specimen was placed slightly in compression to verify that the platen was actually in contact before deformation started.